

AD-A219 385

FILE COPY

4

REPORT No. ONR-9-1 (Final)

PERIOD COVERED: 1 September 1989 through 28 February 1990

NOVEL APPROACHES TO THE SYNTHESIS OF  
FLUORODINITROMETHANE AND FLUORODINITROETHANOL

Contract N00014-89-C-0215  
400o048sbi01/07 JUN 1989/1132P

February 1990

Administered by  
Office of Naval Research, Attn: Richard Miller Code 1132P  
800 North Quincy Street  
Arlington, Virginia 22217-5000

For  
Naval Surface Warfare Center, Attn: H. G. Adolph  
Silver Springs, MD 20903-5000

REPRODUCTION IN WHOLE OR IN PART IS PERMITTED FOR ANY  
PURPOSE OF THE UNITED STATES GOVERNMENT

"Approved for public release; distribution unlimited."

FLUOROCHEM, INC.  
680 South Ayon Avenue  
Azusa, California 91702

DTIC  
ELECTE  
MAR 20 1990  
S B D

109

February 1990

REPORT No. ONR-9-1 (Final)

NOVEL APPROACHES TO THE SYNTHESIS OF  
FLUORODINITROMETHANE AND FLUORODINITROETHANOL

T. G. Archibald, N. Nguyen, J. S. Khosrowshahi and K. Baum

Contract N00014-89-C-0215  
400o048sbi01/07 JUN 1989/1132P

Administered by  
Office of Naval Research, Attn: Richard Miller Code 1132P  
800 North Quincy Street  
Arlington, Virginia 22217-5000

For  
Naval Surface Warfare Center, Attn: H. G. Adolph  
Silver Springs, MD 20903-5000

FLUOROCHEM, INC.

680 South Ayon Avenue  
Azusa, California 91702

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

## REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) ONR-9-1			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Fluorochem, Inc.		6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Naval Surface Warfare Center ATTN: H.G. Adolph		
6c. ADDRESS (City, State, and ZIP Code) 680 S. Ayon Avenue Azusa, CA 91702			7b. ADDRESS (City, State, and ZIP Code) Silver Springs, MD 20903-5000		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-89-C-0215		
8c. ADDRESS (City, State, and ZIP Code) ATTN: Richard Miller, Code 1132P 800 North Quincy Street Arlington, VA 22217-5000			10. SOURCE OF FUNDING NUMBERS		
PROGRAM ELEMENT NO. 400o048		PROJECT NO. sbi01/07	TASK NO.	WORK UNIT ACCESSION NO.	
11. TITLE (Include Security Classification) Novel Approaches to the Synthesis of Fluorodinitromethane and Fluorodinitroethanol					
12. PERSONAL AUTHOR(S) T.G. Archibald, N. Nguyen, J.S. Khosrowshahi and K. Baum					
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM 89AUG15 TO 00FEB15		14. DATE OF REPORT (Year, Month, Day) 90 March 09	
15. PAGE COUNT 42					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Nitration, Fluorocarbons, Fluorodinitroethanol		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Fluorodinitroethanol (FDNE) has been produced without the use of elemental fluorine. Nitration of 1,2-dichlorodifluoroethylene gave chlorofluoronitroacetic acid, which was converted to chlorofluoronitronitrosomethane with red fuming nitric acid and water. Oxidization of the nitroso compound gave chlorofluorodinitromethane, which was reduced to FDNE with iodide in the presence of formaldehyde.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL			22b. TELEPHONE (Include Area Code)		22c. OFFICE SYMBOL

## CONTENTS

INTRODUCTION.....	1
RESULTS AND DISCUSSION.....	2
CONCLUSIONS.....	12
EXPERIMENTAL SECTION.....	13
REFERENCES.....	17

## TABLES

I. CHLOROFLUORONITROACETIC ACID.....	3
II. OXIDATION OF CHLOROFLUORONITRONITROSOMETHANE TO CFDNM.....	7
III. REACTION OF CHLOROFLUORODINITROMETHANE (CFDNM) WITH KI/CH <sub>2</sub> O.....	8
IV. REDUCTIVE DEHALOGENATIONS OF CFDNM IN THE PRESENCE OF FORMALDEHYDE.....	9
V. REDUCTION OF CFDNM.....	11
VI. YIELDS.....	12

<b>Accession For</b>	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
<b>Availability Codes</b>	
Dist	Avail and/or Special
A-1	

## CONTENTS

INTRODUCTION.....	1
RESULTS AND DISCUSSION.....	2
CONCLUSIONS.....	12
EXPERIMENTAL SECTION.....	13
REFERENCES.....	17

## TABLES

I. CHLOROFLUORONITROACETIC ACID.....	3
II. OXIDATION OF CHLOROFLUORONITRONITROSOMETHANE TO CFDNM.....	7
III. REACTION OF CHLOROFLUORODINITROMETHANE (CFDNM) WITH KI/CH <sub>2</sub> O.....	8
IV. REDUCTIVE DEHALOGENATIONS OF CFDNM IN THE PRESENCE OF FORMALDEHYDE.....	9
V. REDUCTION OF CFDNM.....	11
VI. YIELDS.....	12

# FIGURES

1. $^{19}\text{F}$ NMR SPECTRUM OF 1,2-DIFLUOROTETRACHLOROETHANE.....	18
2. $^{19}\text{F}$ NMR SPECTRUM OF 1,2-DICHLORODIFLUOROETHYLENE.....	19
3. $^{13}\text{C}$ NMR SPECTRUM OF CHLOROFLUORONITROACETIC ACID.....	20
4. $^{19}\text{F}$ NMR SPECTRUM OF CHLOROFLUORONITROACETIC ACID.....	21
5. $^{13}\text{C}$ NMR SPECTRUM OF CHLOROFLUORONITROMETHANE.....	22
6. $^{19}\text{F}$ NMR SPECTRUM OF CHLOROFLUORONITROMETHANE.....	23
7. $^{19}\text{F}$ NMR SPECTRUM OF CHLOROFLUORONITRONITROSOMETHANE.....	24
8. $^{13}\text{C}$ NMR SPECTRUM OF CHLOROFLUORODINITROMETHANE.....	25
9. $^{19}\text{F}$ NMR SPECTRUM OF CHLOROFLUORODINITROMETHANE.....	26
10. $^{13}\text{C}$ NMR SPECTRUM OF FLUORODINITROMETHANE.....	27
11. $^{19}\text{F}$ NMR SPECTRUM OF FLUORODINITROMETHANE.....	28
12. $^1\text{H}$ NMR OF FLUORODINITROMETHANE AND FLUORODINITROETHANOL.....	29
13. $^{13}\text{C}$ NMR SPECTRUM OF FLUORODINITROETHANOL.....	30
14. $^{19}\text{F}$ NMR SPECTRUM OF FLUORODINITROETHANOL.....	31
15. $^1\text{H}$ NMR SPECTRUM OF CHLOROFLUORONITROETHANOL.....	32
16. $^{13}\text{C}$ NMR SPECTRUM OF CHLOROFLUORONITROETHANOL.....	33
17. $^{19}\text{F}$ NMR SPECTRUM OF CHLOROFLUORONITROETHANOL.....	34
18. $^{19}\text{F}$ NMR SPECTRUM OF 1,2-DICHLORO-1,2-DIFLUORO-2-NITRO- ETHANOL TRIFLUOROACETATE.....	35
19. $^{19}\text{F}$ NMR SPECTRUM OF 1,2-DICHLORO-1,2-DIFLUORO-2-NITRO- ETHANOL TRIFLUOROMETHANESULFONATE.....	36

## INTRODUCTION

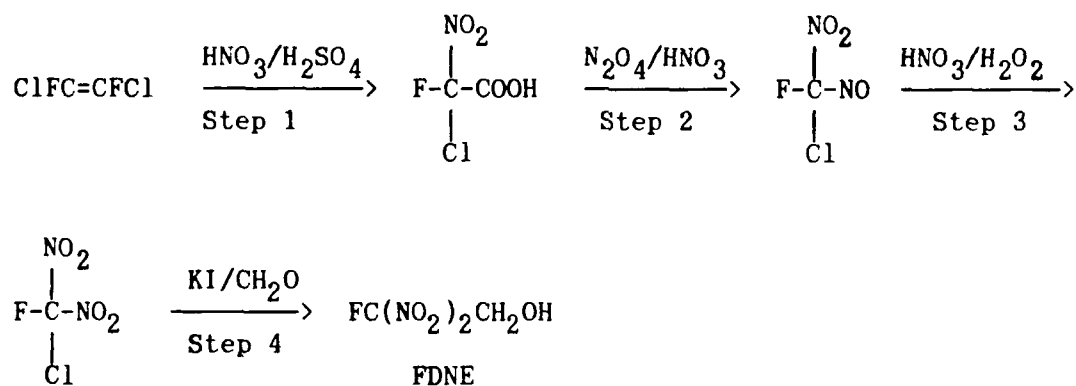
Fluorodinitroethanol (FDNE) is a basic building block for energetic plasticizers and binders. Without compromising thermal stability, FDNE provides greater energy content than dinitropropanol, which has been used in large quantities for manufacture of plasticizers. However, the current production cost limits use of FDNE to special applications, and there is a need for a new, low cost production method. Readily available, inexpensive FDNE and derivative compounds could be used to improve the performance of rocket propellants and explosives.

Two methods<sup>1</sup> have been used previously for manufacturing fluorodinitroethanol and both have significant difficulties. One was based on the fluorination of nitroform and the other on the fluorination of 2,2-dinitropropanediol (A-diol). Nitroform was available at low cost from Sweden until the supply was curtailed by a plant explosion in the 1970's. Environmental and safety problems still inhibit resumption of the large-scale production of nitroform. In the alternate process, A-diol was deformedylated with base and the salt fluorinated. This aqueous fluorination process was complicated by the formation of large amounts of insoluble sodium fluoride, the expense of the A-diol and difficulty in purifying the product. Both of these processes require elemental fluorine, with attendant high plant capital costs.

Prior to this study no practical synthesis of fluorodinitromethyl compounds was known which did not require elemental fluorine or other electrophilic fluorinating reagents. The objective of this Phase I program was to evaluate new approaches to the industrial synthesis of FDNE based on the nitration of inexpensive fluorocarbons.

## RESULTS AND DISCUSSION

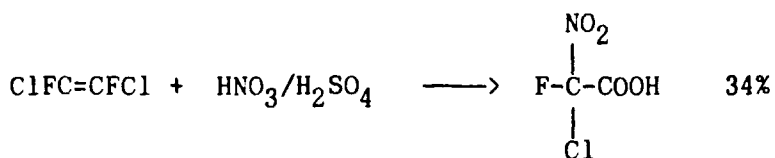
It has been reported in the Russian literature that nitration of 1,2-dichlorodifluoroethylene gives chlorofluoronitroacetic acid, and reaction of the latter with red fuming nitric acid gives chlorofluoronitronitrosomethane. This work was reinvestigated as the basis of an FDNE process. It was expected that oxidation of chlorofluoronitronitrosomethane could give chlorofluorodinitromethane (CFDNM), and that CFDNM could be reduced to give fluorodinitromethane. Fluorodinitromethane is known to react with formaldehyde to give FDNE. These reactions are summarized below.



### Step 1. Nitration of 1,2-Dichlorodifluoroethylene.

We have repeated the reaction of 1,2-dichlorodifluoroethylene with 99% nitric acid and 95% sulfuric acid at room temperature by the procedure of Martynov<sup>2</sup> and have obtained a 34% yield of chlorofluoronitroacetic acid which is comparable to the 36% yield that was reported. The product was isolated from the insoluble organic layer, and assay of the acid layer by <sup>19</sup>F NMR showed the presence of additional product.





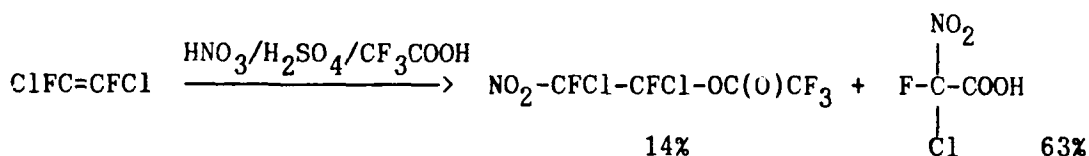
Chlorofluoronitroacetic acid is stable and is readily purified by vacuum distillation at 80°C (10 mm). However, in the presence of water, the acid decarboxylates instantaneously to give chlorofluoronitromethane which was found to be inert to further nitration.

Table I. CHLOROFLUORONITROACETIC ACID

Solvent	Yield	Notes
1. 95% H <sub>2</sub> SO <sub>4</sub> 100% HNO <sub>3</sub>	34%	Some Product in Acid Layer
2. 30% Oleum 100% HNO <sub>3</sub>	44%	
3. 30% Oleum, CF <sub>3</sub> COOH 100% HNO <sub>3</sub>	77%	63% Chlorofluoronitroacetic acid 14% 1,2-Addition Product
4. 95% H <sub>2</sub> SO <sub>4</sub> , CF <sub>3</sub> COOH 100% HNO <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub>	50%	
5. (CF <sub>3</sub> CO) <sub>2</sub> O, CH <sub>2</sub> Cl <sub>2</sub> 100% HNO <sub>3</sub>	60%	22% 1,2-Addition Product
6 30% Oleum, CF <sub>3</sub> SO <sub>3</sub> OH 100% HNO <sub>3</sub>		

Preliminary attempts were made to improve the yield of the nitration reaction. The moisture sensitivity of chlorofluoronitroacetic acid suggested the use of anhydrous reaction conditions, and replacing sulfuric acid with oleum was found to improve the yield to 44%. However, the reaction mixture contained several unidentified fluorinated material with <sup>19</sup>F NMR signals in the δ -50 to -70 range. In reactions without nitric acid, the olefin has been reported to react with oleum to give high yields of the corresponding cyclic sulfone.<sup>3</sup>

Chlorofluoronitroacetic acid was obtained in 63% yield when a mixture of oleum, nitric acid and trifluoroacetic acid was reacted with 1,2-dichlorodifluoroethylene. The 1,2-addition product, 1,2-dichloro-1,2-difluoro-2-nitroethyl trifluoroacetate, was isolated in 14% yield, bringing the effective yield of nitration to 77%. Apparently the 1,2-addition product was formed first and then was hydrolyzed *in situ*, to give the acetic acid derivative. The lower boiling point and diminished water sensitivity of the 1,2-addition product makes it a potentially attractive alternative to chlorofluoronitroacetic acid in subsequent nitration reactions.



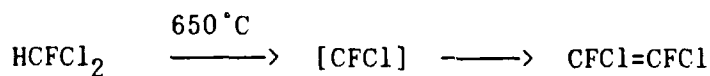
This nitration in a mixture of sulfuric, nitric and trifluoroacetic acids in methylene chloride gave a 50% yield of chlorofluoronitroacetic acid on the basis of  $^{19}\text{F}$  NMR assay. Similar nitration with  $\text{N}_2\text{O}_5$  prepared from trifluoroacetic anhydride and nitric acid in methylene chloride gave a 60% yield of chlorofluoronitroacetic acid. When a mixture of nitric acid, oleum and triflic acid was used as the nitration medium, the 1,2-addition product 1,2-dichloro-1,2-difluoro-2-nitroethyl triflate was isolated 22% yield, but only trace amounts of chlorofluoronitroacetic acid were formed.

Variables such as reaction temperature, order of addition, concentration and methods of isolation on the yields of the nitration reactions were not investigated extensively. Since nitrations of other fluoroolefins such as tetrafluoroethylene<sup>4</sup> give yields as high as 92% of the corresponding nitro-

acetic acids, it is probable that under optimum conditions, 1,2-dichlorodifluoroethylene can be converted to chlorofluoronitroacetic acid in yields exceeding 77%.

The 1,2-dichlorodifluoroethylene used in this study was either purchased from PCR or prepared in 80% yield from commercially available 1,2-difluorotetrachloroethane by zinc mediated reduction.<sup>5</sup> The olefin from both sources was identical and was found to be an equal mixture of *cis* and *trans* isomers of 1,2-difluorotetrachloroethane, contaminated by 10% of 1,1-difluorodichloroethylene. Yields in this report were corrected for the presence of the latter isomer. The source of the unsymmetrical isomer was found to be a 10% impurity of 1,1-difluorotetrachloroethane in the 1,2-difluorotetrachloroethane used as the starting material.

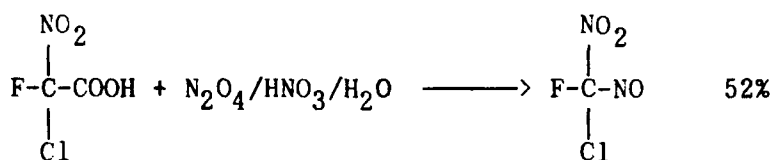
The presence of the 1,1-difluoro isomer in the starting material presented the potential problem that nitration might lead to formation of a highly toxic byproduct, difluoronitroacetic acid. This acid, however, was not detected in the product mixtures. The problem can be avoided by using another synthesis of 1,2-dichlorodifluoroethylene; the pyrolysis of fluorodichloromethane<sup>6</sup> has been reported to give pure 1,2-dichlorodifluoroethylene in a process similar to that used in the manufacture of tetrafluoroethylene.



#### Step 2. Chlorofluoronitronitrosomethane.

Chlorofluoronitroacetic acid is decarboxylated rapidly in the presence of water to give chlorofluoronitromethane. However, it has been reported that

the decarboxylation reaction in the presence of fuming nitric acid gave a nitroso compound.<sup>7</sup> During this program, we repeated this reaction and isolated a 51% yield of chlorofluoronitronitrosomethane; the reported yield was 52%. The reaction was conducted at 80°C in 90% nitric acid containing 20% N<sub>2</sub>O<sub>4</sub> and chlorofluoronitronitrosomethane was distilled from the reaction mixture as an intensely blue liquid contaminated with N<sub>2</sub>O<sub>4</sub>. The yield was confirmed by <sup>19</sup>F NMR using trifluorotoluene an internal reference. This intermediate was stable for several days at ambient temperature, but was generally used directly in the next step without further isolation or purification.



A possible route for this reaction consists of decarboxylation of chlorofluoronitroacetic acid to give chlorofluoro-*acit*-nitromethane, followed by nitrosation by oxides of nitrogen to give chlorofluoronitronitrosomethane. Reaction of other *acit*-nitro compounds with N<sub>2</sub>O<sub>4</sub> to give pseudonitroles under similar conditions has been reported.<sup>8</sup> The reaction of 1,2-dichlorodifluoroethylene with fuming nitric acid did not give chlorofluoronitronitrosomethane, but when the mixture was diluted with water, the nitronitroso compound was formed in 24% yield. This result suggests that nitration conditions may be found to combine step 1 and step 2 into a one-pot reaction.

### Step 3. Chlorofluorodinitromethane

Oxidation of chlorofluoronitronitrosomethane with 30% hydrogen peroxide

in nitric acid at ambient temperature gave chlorofluorodinitromethane in 62% isolated yield. The reaction was 90% complete after 15 minutes (See Table II).

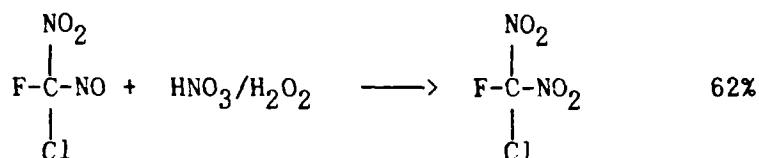
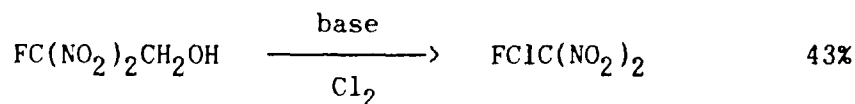


Table II. OXIDATION OF CHLOROFLUORONITRONITROSOMETHANE TO CFDNM

Time, min	ClFC(NO <sub>2</sub> )NO %	ClFC(NO <sub>2</sub> ) <sub>2</sub> %
0	100	0
15	10.8	56.7
30	8.2	61.7
45	5.1	60

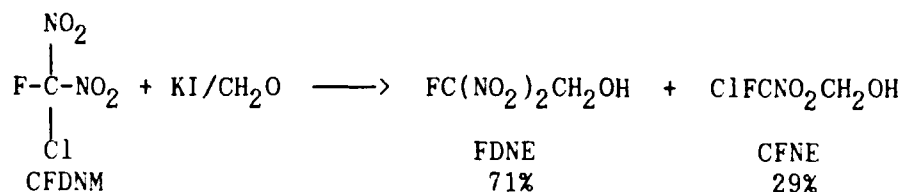
Chlorofluorodinitromethane was first prepared by the direct aqueous fluorination of potassium chlorodinitromethane<sup>9</sup> and more recently by the unusual reaction of chlorofluoronitroacetic acid with xenon difluoride.<sup>10</sup> To obtain a reference sample for this program, authentic chlorofluorodinitromethane was synthesized by the reaction of FDNE with aqueous bleach in 43% yield.



#### Step 4. Reduction of CFDNM to FDNE.

FDNE has been prepared by reduction of fluorotrinitromethane with sodium hydroxide and hydrogen peroxide in the presence of formaldehyde.<sup>1</sup> Attempted reduction of CFDNM under these conditions resulted in substantial hydrolysis to fluoride ion and the formation of small amounts of chlorofluoro-

nitroethanol.<sup>11</sup> Only trace amounts of FDNE were produced either in aqueous solution or when alcohols were used as cosolvents.



However, yields of FDNE as high as 71% were realized when KI was used as the reducing agent. Results using a 30% aqueous ethanolic solution of CFDNM (1 eq), KI (2.3 eq) and 30% formaldehyde solution (1.3 eq) at 70°C are summarized in the Table III. Formation of both FDNE and chlorofluoronitroethanol (CFNE) was observed with the maximum amount of FDNE observed at 1 h reaction time.

Table III. REACTION OF CHLOROFLUORODINITROMETHANE (CFDNM) WITH KI/CH<sub>2</sub>O

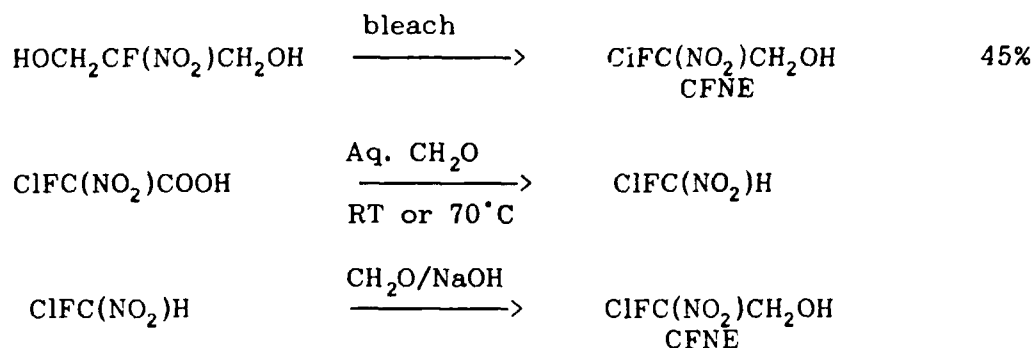
Time at 70°C min	CFDNM %	FDNE %	CFNE %	F <sup>-</sup> %
0	100	-	-	-
30	9.0	56.5	18.8	1.8
60	4.7	66.6	23.8	2.8
90	3.6	63.1	24.8	4.9
120	3.0	60.2	25.7	4.9

Other reaction variations are summarized in Table IV. The reaction with KI was found to be slow at room temperature, with less than 10% of the CFDNM reduced after 3 hours. Reactions conducted at 40 to 75°C for short periods and then continued for several days at room temperature gave the best results. When the reaction temperature exceeded 75°C, no FDNE was formed and complete hydrolysis to fluoride ion occurred.

Table IV. REDUCTIVE DEHALOGENATIONS OF CFDNM IN THE PRESENCE OF FORMALDEHYDE

Protocols	Products (Yields from <sup>19</sup> F NMR integration)			
	CFDNM	FDNE	CFNE	F <sup>-</sup>
H <sub>2</sub> O <sub>2</sub> /NaOH/CH <sub>2</sub> O in water 0°C, 1 h	trace	trace	5%	95%
H <sub>2</sub> O <sub>2</sub> /NaOH/CH <sub>2</sub> O in aq. MeOH 0°C for 1 h then RT for 1 h	5%	none	2%	95%
H <sub>2</sub> O <sub>2</sub> /NaOH/CH <sub>2</sub> O in aq. EtOH 0°C for 1 h then RT for 1 h	40%	trace	trace	60%
KI/CH <sub>2</sub> O in aq. EtOH 3 h at RT	90%	5%	5%	none
then 2 days at RT	8%	50%	34%	5%
KI/CH <sub>2</sub> O in aq. EtOH 2 h at 40°C	33%	44%	23%	none
then 2 days at RT	none	71%	29%	trace
KI/CH <sub>2</sub> O in aq. EtOH 1/2 h at 75°C	15%	58%	24%	3%
then 2 days at RT	none	67%	30%	3%
KI in aq. EtOH 1/2 h at 75°C	none	none	trace	99%

Small amounts of chlorofluoronitroethanol (CFNE) were observed as a byproduct in most KI reductions. The boiling point of CFNE (40°C/0.4 mm) is close to that of FDNE (41°C/0.1 mm) and these materials could not be separated readily by distillation. Pure chlorofluoronitroethanol was prepared for use as a reference standard by chlorination of 2-fluoro-2-nitro-1,3-propanediol in 45% yield. CFNE was also prepared in small yield by decarboxylation of chlorofluoronitroacetic acid in aqueous formaldehyde.



In an effort to eliminate CFNE formation, several other reduction conditions were investigated. Fluorotrinitromethane reacts with aqueous formaldehyde solution to give FDNE in 36% yield in the absence of other reducing agents.<sup>12</sup> However, under similar conditions, CFDNM failed to give FDNE. Other reactions of CFDNM with various "soft" nucleophiles and reducing agents are summarized in Table V below. The best results were obtained with sodium sulfide and sodium thiosulfate. However, sodium sulfide also reacted with formaldehyde to give insoluble trithiane. At room temperature, even after 16 h, these reactions were not complete. The reaction mixture containing sodium thiosulfate gave two phases after it was heated at 70°C for 10 h. The aqueous phase showed only FDNE and the organic phase showed several unidentified products in addition to FDNE.



Table V. REDUCTION OF CFDNM

	Temp	FDNE	CFNE	F <sup>-</sup>	Comments
KBr	RT	-	-		no rxn
	70°C	-	-		no rxn
CH <sub>3</sub> COOK	RT	-	-		no rxn
	70°C	-	-		no rxn
NaNO <sub>2</sub>	RT	-	-		no rxn
	70°C	-	-		no rxn
Na <sub>2</sub> SO <sub>3</sub>	RT	-	-		no rxn
	70°C	-	-		no rxn
K <sub>3</sub> Fe(CN) <sub>6</sub>	RT	-	-		no rxn
	70°C	-	-		no rxn
KOCN	RT	-	-		no rxn
	70°C	2%	5%	16%	unreacted CFDNM
KCN	RT	22%	18%	17%	unreacted CFDNM
	70°C	7%	50%	40%	
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	RT	60%	trace	trace	unreacted CFDNM
KSCN	RT	-	-		no rxn
	70°C	35%	trace		unreacted CFDNM solid in rxn mixt
Na <sub>2</sub> S	RT	30%	trace	40%	unreacted CFDNM
	70°C	50%	7%	40%	water insoluble solid in mixt

## CONCLUSIONS

The feasibility of a new synthetic route to FDNE based on the nitration of 1,2-dichlorodifluoroethylene has been demonstrated during this Phase I program. This work shows that direct fluorination is not necessary for the synthesis of the fluorodinitromethyl group.

Nitration of 1,2-dichlorodifluoroethylene gave chlorofluoronitroacetic acid,

which was converted to chlorofluoronitronitrosomethane with red fuming nitric acid and water. Oxidization of the nitroso compound gave CFDNM, which was reduced to FDNE with iodide. This new sequence has the potential to provide low-cost FDNE on an industrial scale in an environmentally acceptable process. Since the first three steps involve variations of reactions in nitric acid, it is possible that a one-pot reaction can be developed. Optimum reaction conditions have not been established, but the best results during this program are summarized in Table VI.

Table VI. YIELDS OF REACTIONS LEADING TO FDNE.

STEP	STARTING MATERIAL	PRODUCT	YIELD
1.	$\text{ClFC}=\text{CFCl}$	$\text{ClFCNO}_2\text{COOH}$	77%
2.	$\text{ClFCNO}_2\text{COOH}$	$\text{ClFCNO}_2\text{NO}$	52%
3.	$\text{ClFCNO}_2\text{NO}$	$\text{ClFC}(\text{NO}_2)_2$ (CFDNM)	62%
4.	$\text{ClFC}(\text{NO}_2)_2$	$\text{FC}(\text{NO}_2)\text{CH}_2\text{OH}$ (FDNE)	71%

## EXPERIMENTAL

IR spectra were recorded in  $\text{CH}_2\text{Cl}_2$  on a Perkin-Elmer 700 spectrometer.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded in  $\text{CDCl}_3$  on a Bruker AC200 spectrometer and are reported in ppm relative to TMS and  $\text{FCCl}_3$ . Warning: Fluorodinitroethanol is a powerful skin irritant.

**1,2-Dichlorodifluoroethylene:** A suspension of zinc powder (144 g, 2.2 mol) and zinc chloride (0.1 mg) in ethanol (200 mL) was stirred mechanically in a 2-L three neck flask equipped with a 12" vigreux column, fraction splitter, and a condenser cooled to  $-20^\circ\text{C}$ . Approximately 20 mL of a solution of 1,1- and 1,2-difluorotetrachloroethanes (240 g, 1.17 mol, 1:9 mixture) in ethanol (40 mL) was added and the mixture was heated to  $45\text{--}55^\circ\text{C}$ . The remainder of the solution was added dropwise over 4 h, while the product was distilled at  $18\text{--}20^\circ\text{C}$  through the column operated at a 1:1 reflux ratio and collected in a receiver cooled to  $-78^\circ\text{C}$ . The resulting distillate contained 125 g (80%) of a mixture of *cis*- and *trans*-1,2-dichlorodifluoroethylene and 1,1-difluorotetrachloroethane (45:45:10 ratio by  $^{19}\text{F}$  NMR): No signals in  $^1\text{H}$  NMR;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -119.6 (s, *trans*-isomer), -105.1 (s, *cis*-isomer), and -88.5 (1,1-dichlorodifluoroethylene).<sup>13</sup> This material was identical to that obtained commercially.

**Chlorofluoronitroacetic Acid, Sulfuric Acid Procedure.** A solution of 100%  $\text{HNO}_3$  (30 mL) in conc.  $\text{H}_2\text{SO}_4$  (35 mL) was added over 30 min to neat 1,2-dichlorodifluoroethylene (48 g, 0.35 mol) at  $10\text{--}15^\circ\text{C}$ ; an exothermic reaction was observed. The mixture was stirred for 10 min at  $10^\circ\text{C}$ . The organic layer was separated, and distilled to give 14 g (34%) of chlorofluoronitroacetic acid, bp  $45\text{--}65^\circ\text{C}$  (0.5 mm) (Lit<sup>2</sup> bp  $90^\circ\text{C}$  / 8 mm):  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -89.71;  $^{13}\text{C}$  NMR  $\delta$  113.69 (d,  $J = 303$  Hz), 161.21 (d,  $J = 29$  Hz).

**Chlorofluoronitroacetic Acid, Oleum Procedure.** A solution of 100% nitric acid (9 mL) in 30% oleum (11 mL) was added over 25 min to 1,2-dichlorodifluoroethylene (13.3 g, 0.1 mol) at 14-17°C. The mixture was stirred for 30 min at 10-14°C. The organic layer was separated, and distilled to give 6.84 g (44%) of chlorofluoronitroacetic acid, bp 80-85°C (8 mm), identical to the material prepared above.

**Chlorofluoronitroacetic Acid, Oleum-Trifluoroacetic Acid Procedure.** A solution of 100% nitric acid (5 mL) and trifluoroacetic acid (4.2 mL, 54 mmol) in 30% oleum (6 mL) was added over 25 min to 1,2-dichlorodifluoroethylene (7.5 g, 56 mmol) at 10-15°C. The mixture was stirred for 60 min at 10-14°C. The organic layer was separated, and fractionally distilled to give 2.1 g (14.5%) of 1,2-dichloro-1,2-difluoro-1-nitroethyl trifluoroacetate, as a 50:50 mixture of diastereomers, bp 48-50°C (0.5 mm):  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -76.27 (s, 6 F), -77.50 (s, 1 F), -78.49 (s, 1F), -94.37 (s, 1 F), -95.30 (s, 1 F). The second fraction contained 4.0 g of chlorofluoronitroacetic acid, bp 55-65°C (0.5 mm), identical to the authentic material prepared above. The oleum layer was heated to 80°C under vacuum (0.5 mm) to give an additional 1.61 g (63% combined yield) of chlorofluoronitroacetic acid.

**Chlorofluoronitroacetic Acid, Oleum-Triflic Acid Procedure.** A solution of 100% nitric acid (5.5 mL) and trifluoromethanesulfonic acid (5.6 mL, 63 mmol) in 30% oleum (6.5 mL) was added over 30 min to 1,2-dichlorodifluoroethylene (8.4 g, 63 mmol) at 10-15°C. The mixture was stirred for 60 min at 10-14°C. The organic layer was separated, and distilled to give 4.9 g (24%) of 1,2-dichloro-1,2-difluoro-1-nitroethyl trifluoromethanesulfonate, bp 60-65°C (0.5 mm), as a 50:50 mixture of diastereomers:  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -68.47 (s, 1 F), -69.60 (s, 1 F), -73.32 (s, 6 F,  $\text{OSO}_2\text{CF}_3$ ), -92.84 (s, 1 F), -93.52 (s, 1 F).

**Chlorofluoronitronitrosomethane.** Red fuming  $\text{HNO}_3$  (7 mL) was added to a mixture of chlorofluoronitroacetic acid (2.4 g, 15.3 mmol) and water (2 mL). The mixture was heated to  $100^\circ\text{C}$  and the distillate boiling at  $45\text{--}92^\circ\text{C}$  was collected until the reaction mixture ceased to be blue in color. The blue distillate contained a mixture of  $\text{N}_2\text{O}_4$  and 1.1 g (51%) of chlorofluoronitronitrosomethane (assayed by  $^{19}\text{F}$  NMR using trifluorotoluene as the internal standard.)  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -85.8 (t,  $J = 10$  Hz) (Lit<sup>7</sup> -85.6).

**Chlorofluorodinitromethane from Fluorodinitroethanol.** A solution of KOH (24.7 g, 0.44 mol) in bleach (12.5%  $\text{NaClO}$  solution, 400 mL) was added to a solution of fluorodinitroethanol (67.8 g, 0.44 mol) in water (100 mL) at  $0\text{--}5^\circ\text{C}$ . The mixture was stirred at  $0^\circ\text{C}$  for 15 min and the layers were separated. The aqueous layer was extracted with methylene chloride (3 X 50 mL) and the combined organic layers were washed with 100 mL of brine and dried ( $\text{MgSO}_4$ ). The solvent was evaporated and the residue was distilled to give 29.4 g (43% yield) of chlorofluorodinitromethane, bp  $70\text{--}80^\circ\text{C}$  (Lit bp  $83\text{--}84^\circ\text{C}$  / 747 mm);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , Freon 113)  $\delta$  -67.75 (q,  $J = 11.1$  Hz) (Lit<sup>14</sup> -67.68);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  122.5 (2 x 5,  $J_{\text{CF}} = 333.4$  Hz,  $J_{\text{CN}} = 11.9$  Hz).

**Chlorofluorodinitromethane from Chlorofluoronitronitrosomethane.** A solution of chlorofluoronitronitrosomethane (3.8 mg, 0.027 mmol) in 0.5 mL of  $\text{CDCl}_3$  in an NMR tube was cooled to  $5^\circ\text{C}$  and 0.2 mL of 100%  $\text{HNO}_3$  and 0.1 mL of 30%  $\text{H}_2\text{O}_2$  solution were added. The temperature was kept at  $5^\circ\text{C}$  until the exothermic reaction subsided. The solution was then shaken at room temperature for 0.5 h until the blue color disappeared. The residue contained 2.5 mg (62% yield) of chlorofluorodinitromethane by  $^{19}\text{F}$  NMR analysis (trifluorotoluene internal standard). This material was identical to authentic chlorofluorodinitromethane prepared above.

**Fluorodinitroethanol from Chlorofluorodinitromethane.** A solution of chlorofluorodinitromethane (0.95 g, 6.0 mmol), KI (2.5 g, 15 mmol), and 37% aqueous formaldehyde (0.6 mL, 7 mmol) in 30% aqueous ethanol (10 mL) was heated at 70°C for 1 h. The solution was cooled and was found to contain 0.62 g (67%) of fluorodinitroethanol and 0.19 g (23%) of chlorofluoronitroethanol by  $^{19}\text{F}$  NMR assay (trifluoroethanol internal standard).

**Chlorofluoronitroethanol.** A solution of 2-fluoro-2-nitro-1,3-propanediol (3.0 g, 21.6 mmol) in of 12.5% bleach ( $\text{NaClO}$ , 100 mL) was stirred at ambient temperature for 3 h and then extracted with methylene chloride (2 X 100 mL). The combined organic solutions were dried ( $\text{MgSO}_4$ ) and filtered through a pad of silica gel, and evaporated to give a yellow oil. The residual oil was distilled to give 1.3 g (42%) of chlorofluoronitroethanol, bp 39–40°C (0.4 mm):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.58 (b, 1H), 4.16–4.49 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  62.29 (d,  $J$  = 23.7 Hz), 119.97 (d,  $J$  = 293.2 Hz);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -98.19 (dd,  $J$  = 6.8, 22 Hz). Anal. Calcd for  $\text{C}_2\text{H}_3\text{ClFNO}_2$ : C, 16.74; H, 2.11; N, 9.76. Found: C, 16.72; H, 2.37; N, 9.68.

# REFERENCES:

1. (a) Kamlet, M. J.; Adolph, H. G. J. Org. Chem. 1968, 33, 3073.  
(b) Grakauskas, V.; Baum, K. J. Org. Chem. 1968, 33, 3080.
2. Martynov, I. V.; Kruglyak, Y. L.; Markarov, S. P. Zh. Obshch. Khim., 1963 33, 3384 (Eng. Trans. p. 3311)
3. Sokolskii, G. A.; Knunyants, I. L. Izv. Akad. Nauk SSSR, Ser. Khim. 1965, 1655 (Eng. transl. p. 1611.)
4. Martynov, I. V.; Kruglyak, Y. L.; Privezenstseva, N. F. Zh. Org. Khim. 1969, 5, 432 (Eng. transl. p. 420.)
5. Locke, E. G.; Brode, W. R.; Henne, A. L. J. Am. Chem. Soc. 1934, 56, 1726.
6. (a) Makoto, H. Nippon Kagaku Kaishi 1979, 302; C.A. 1980, 90, 169024e.  
(b) USP 2,551,573 (1945) to Dupont, Inc.
7. Martynov, I. V.; Brel', V. K.; Uvarova, L. V. Izv. Akad. Nauk SSSR, Ser. Khim., 1986, (4), 953 (Eng. Trans. p. 870.)
8. Noland, W. E.; Libers, R. Tetrahedron, 1963, 19, Suppl. 1, 23.
9. Fokin, A. V.; Galakhov, V. S.; Radchenko, V. P. Zh. Obshch. Khim. 1969, 39, 1605 (Eng. Trans. p. 1573).
10. Martynov, I. V.; Brel', V. K.; Uvarov, V. I.; Pomytkin, I. A.; Aleinikov, N. N.; Kashtanov, S. A. Izv. Akad. Nauk SSSR, Ser. Khim. 1988, (2) 466 (Eng. Trans p 386).
11. L'vova, M. S.; Slovetetskii, V.I.; Okhlobystina, L. V.; Khutoretskii, V. M.; Fainzil'berg, A. A. Izv. Akad. Nauk SSSR, Ser. Khim. 1971, 95 (Eng. Trans. p. 80.)
12. Fridman, A. L.; Ivsnina, T. N.; Ivsnin, V. P.; Senichev, Y. N. Zh. Obshch. Khim., 39, 1969, 1181.
13. Renben, J. Demiel, A. J. Chem. Phys. 1966, 44, 2216.
14. Kessenikh, A. V.; Okhlobystina, L. V.; Khutoretskii, V. M.; Fainzil'berg, A. A.; Babushkina, T. A.; Semin, G. K. Teor. Eksper. Khim., 5, 1969, 426.

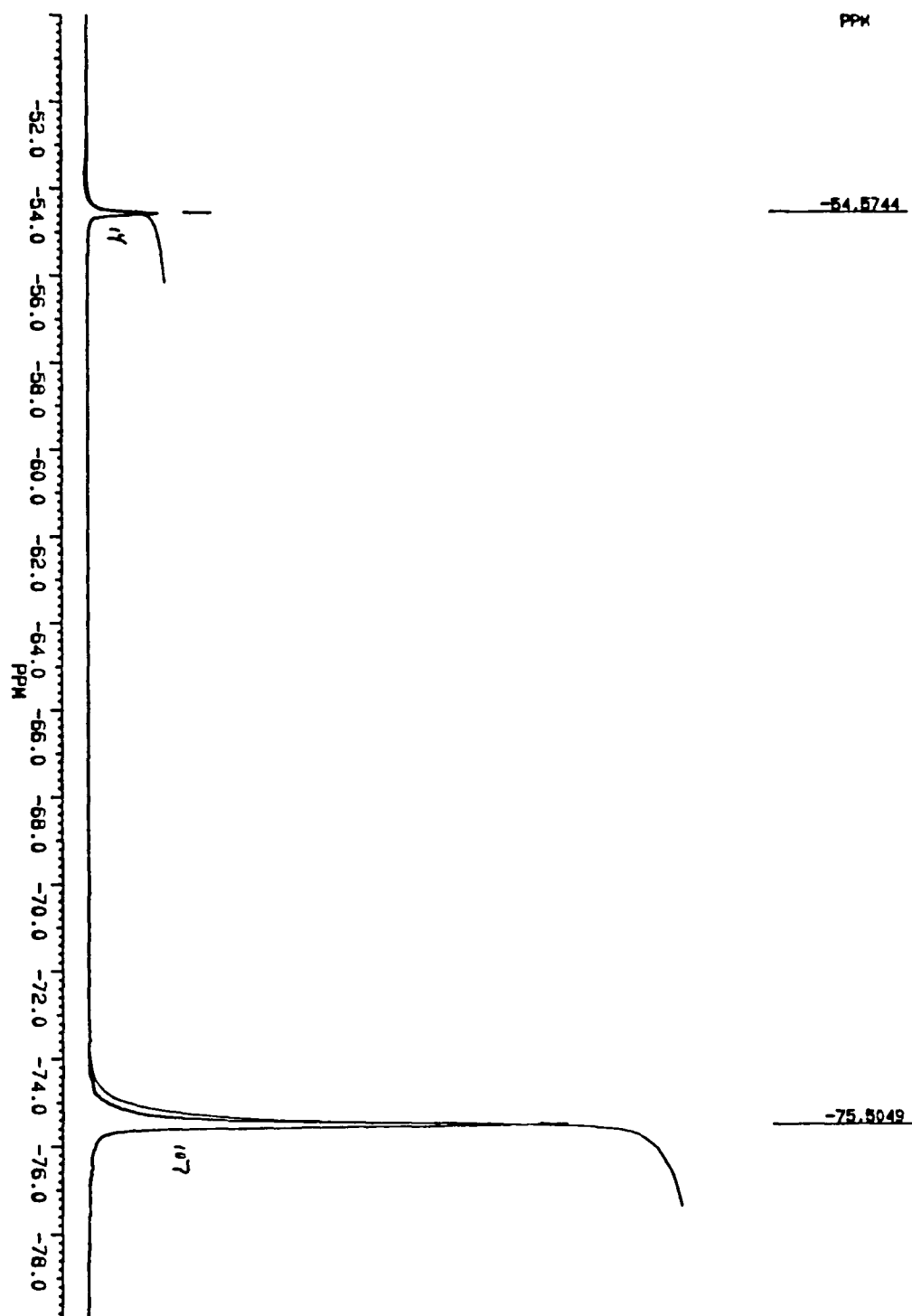
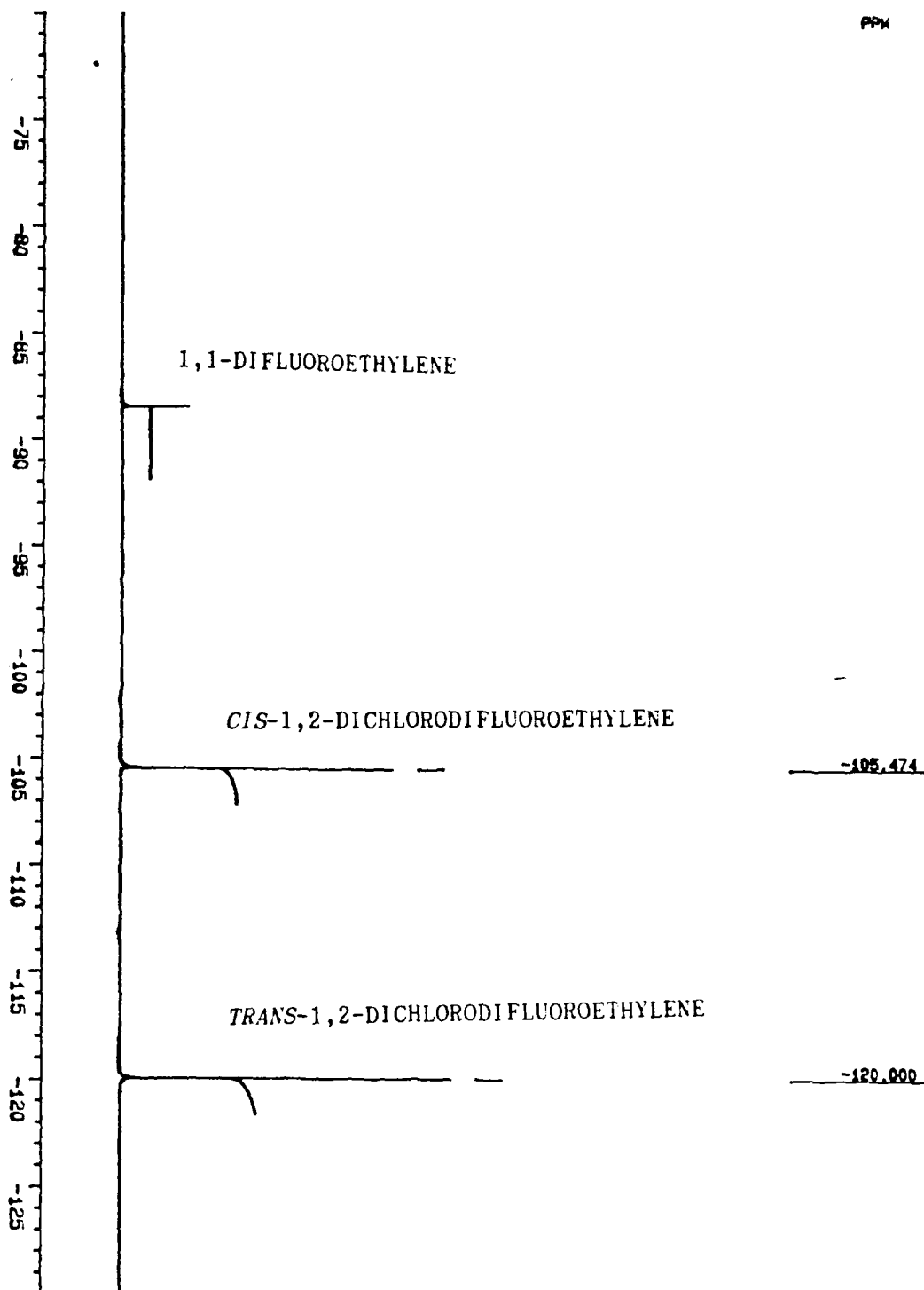


FIGURE 1.  $^{19}\text{F}$  NMR SPECTRUM OF 1,2-DIFLUOROTETRACHLOROETHANE (PCl<sub>2</sub>)



FIGURE 2.  $^{19}\text{F}$  NMR SPECTRUM OF 1,2-DICHLORODIFLUOROETHYLENE



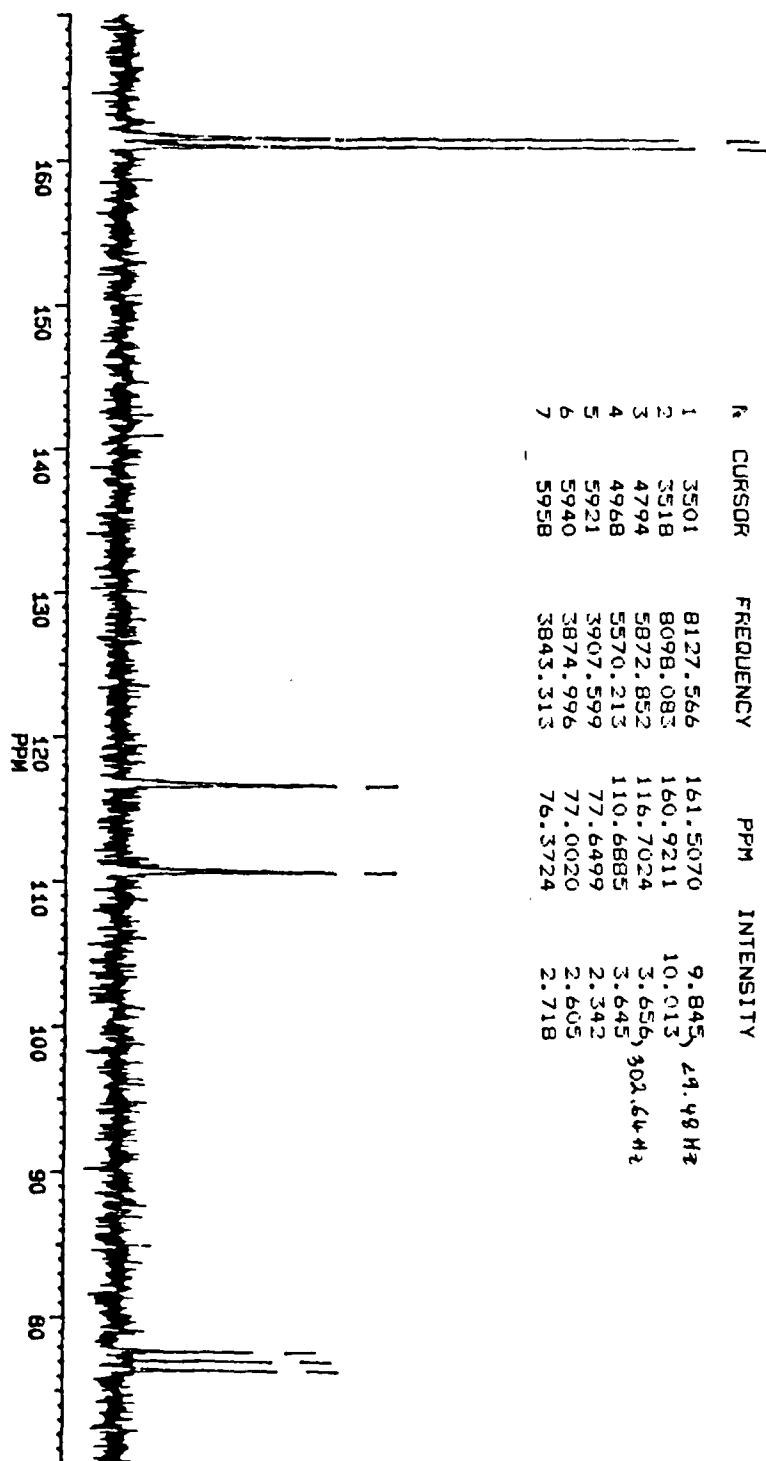


FIGURE 3.  $^{13}\text{C}$  NMR SPECTRUM OF CHLOROFUORONITROACETIC ACID

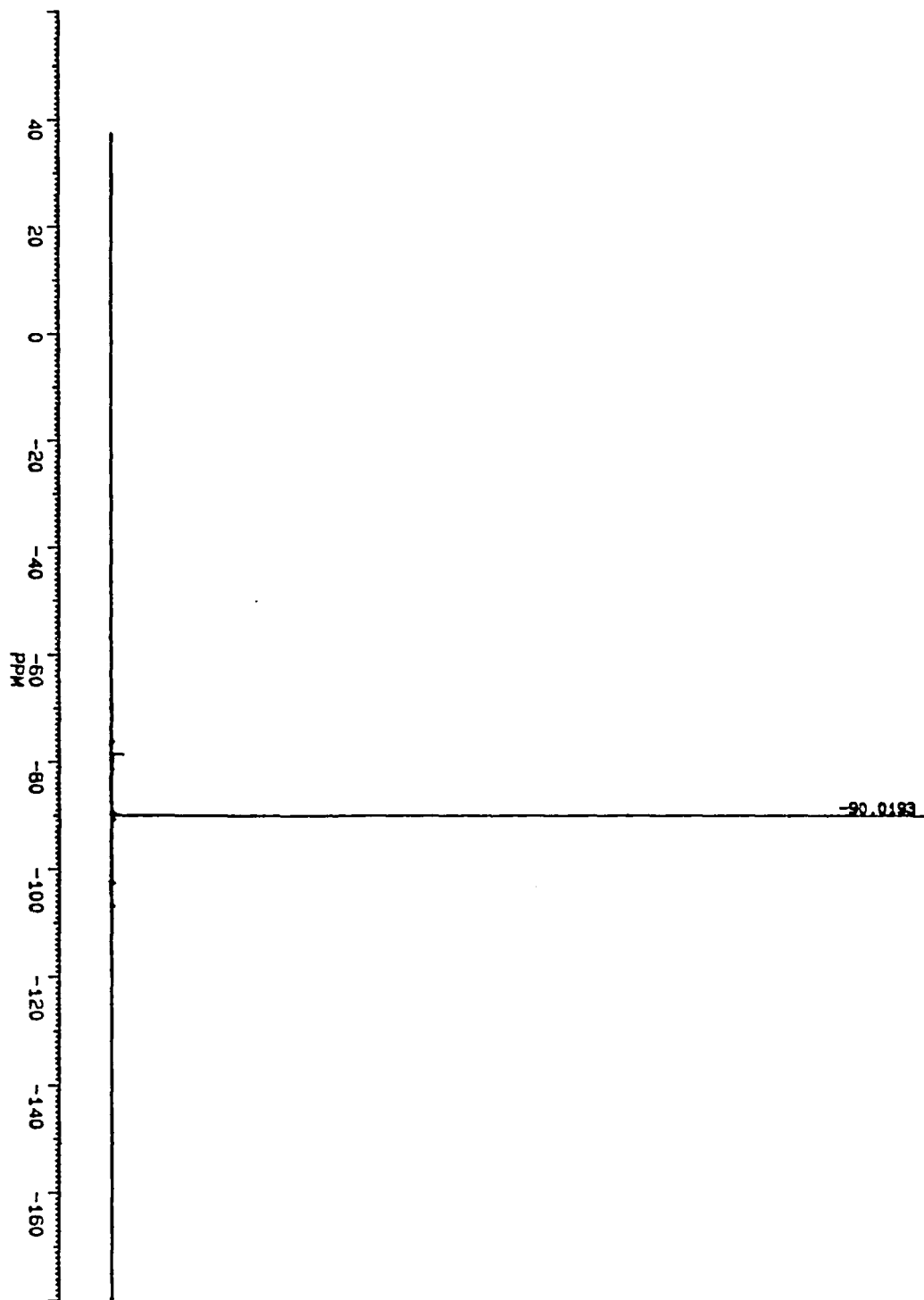


FIGURE 4.  $^{19}\text{F}$  NMR SPECTRUM OF CHLOROFLUORONITROACETIC ACID

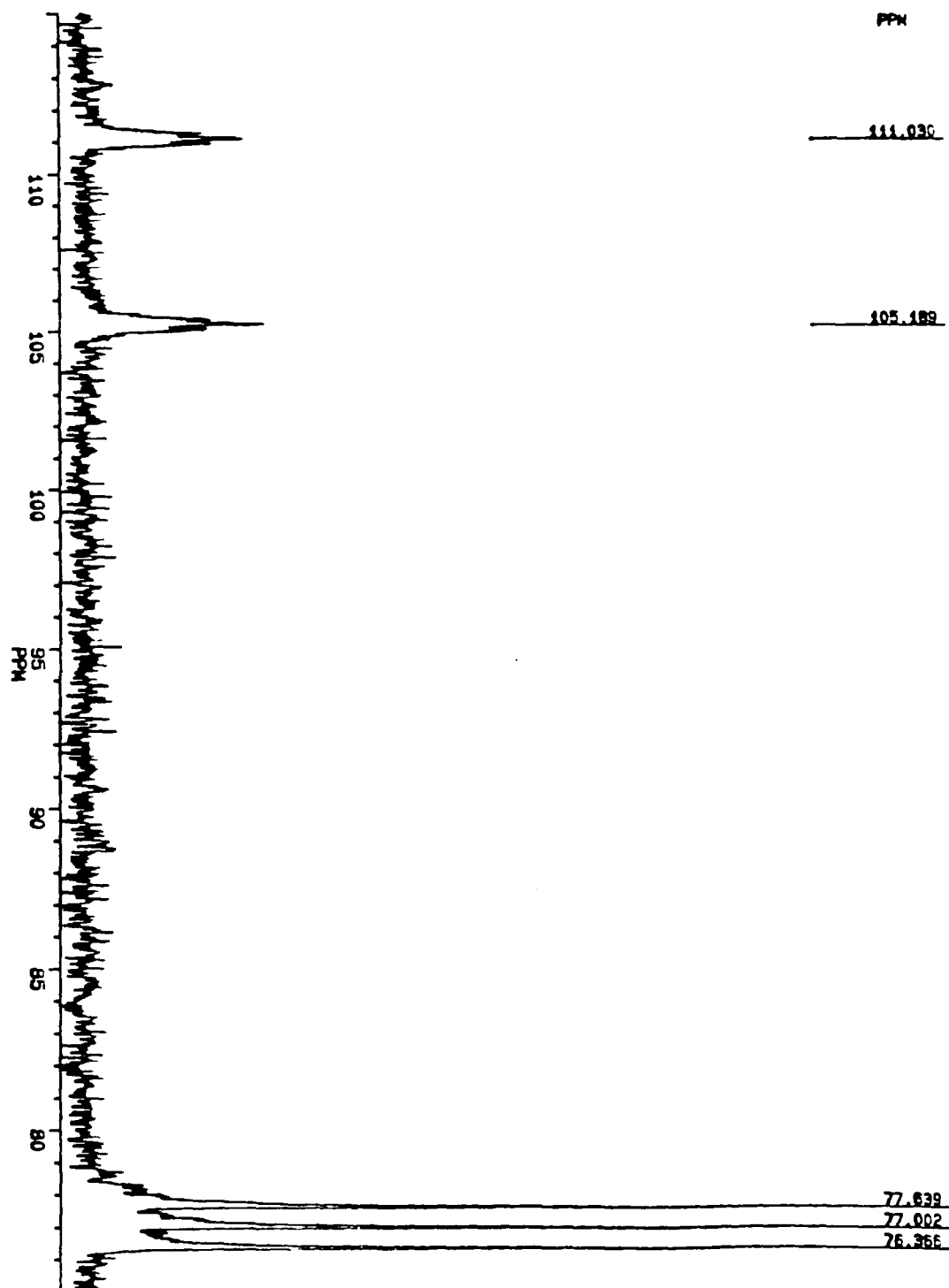


FIGURE 5.  $^{13}\text{C}$  NMR SPECTRUM OF CHLOROFUORONITROMETHANE

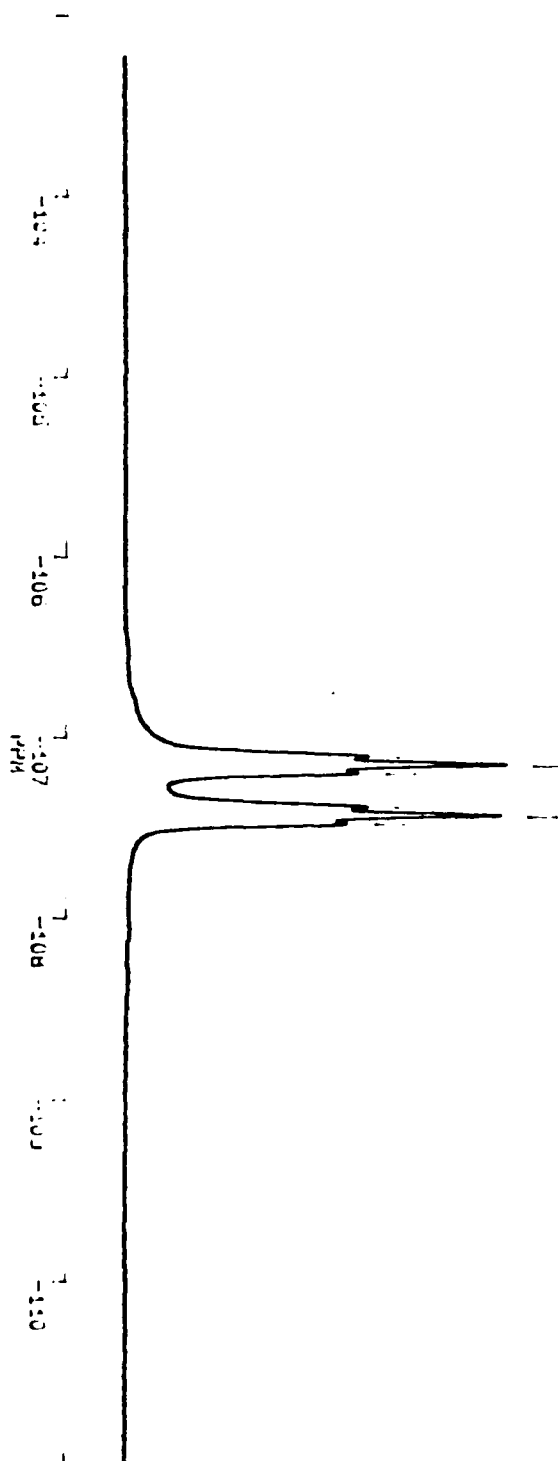


FIGURE 6.  $^{19}\text{F}$  NMR SPECTRUM OF CHLOROFUORONITROMETHANE

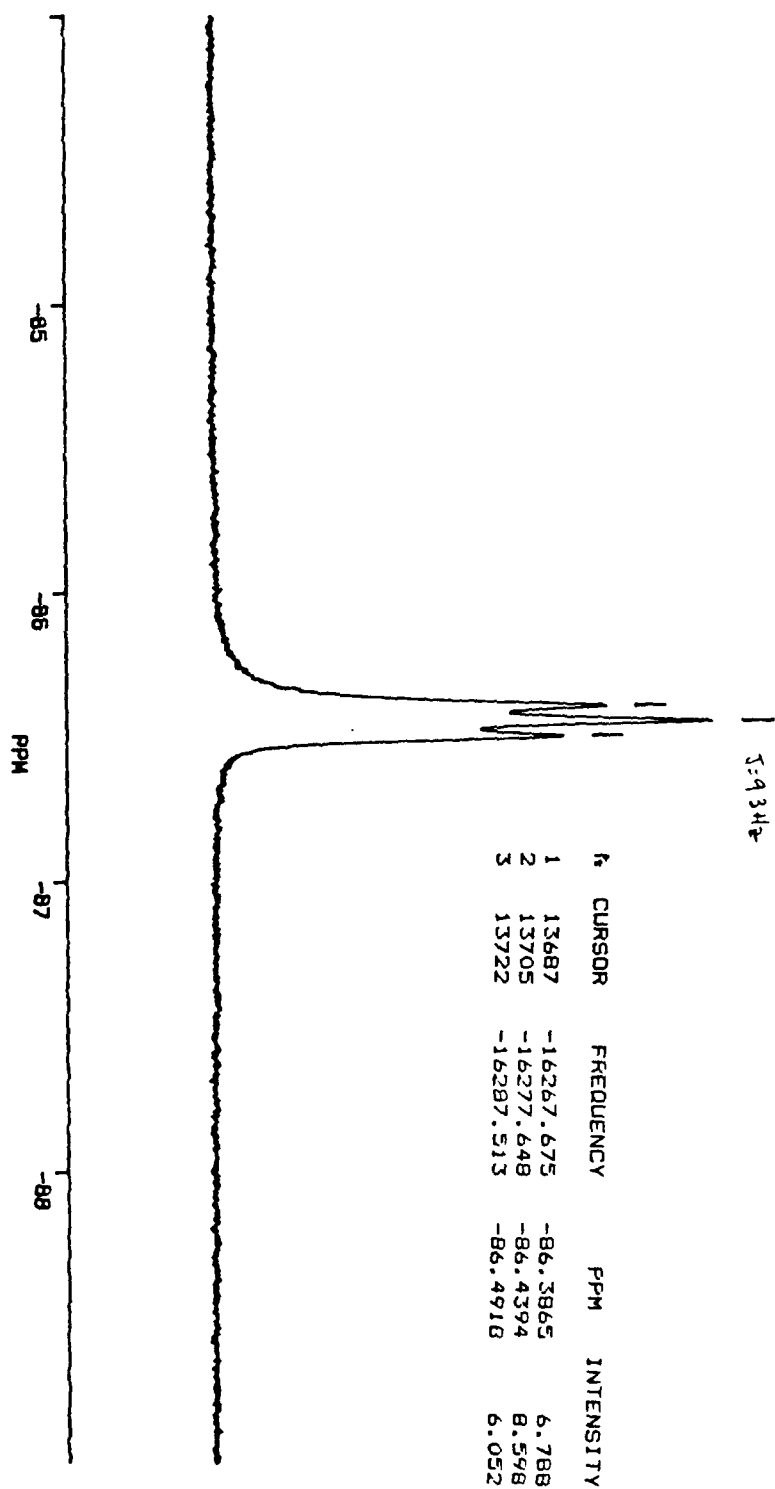


FIGURE 7.  $^{19}\text{F}$  NMR SPECTRUM OF CHLOROFUORONITRONITROSOMETHANE

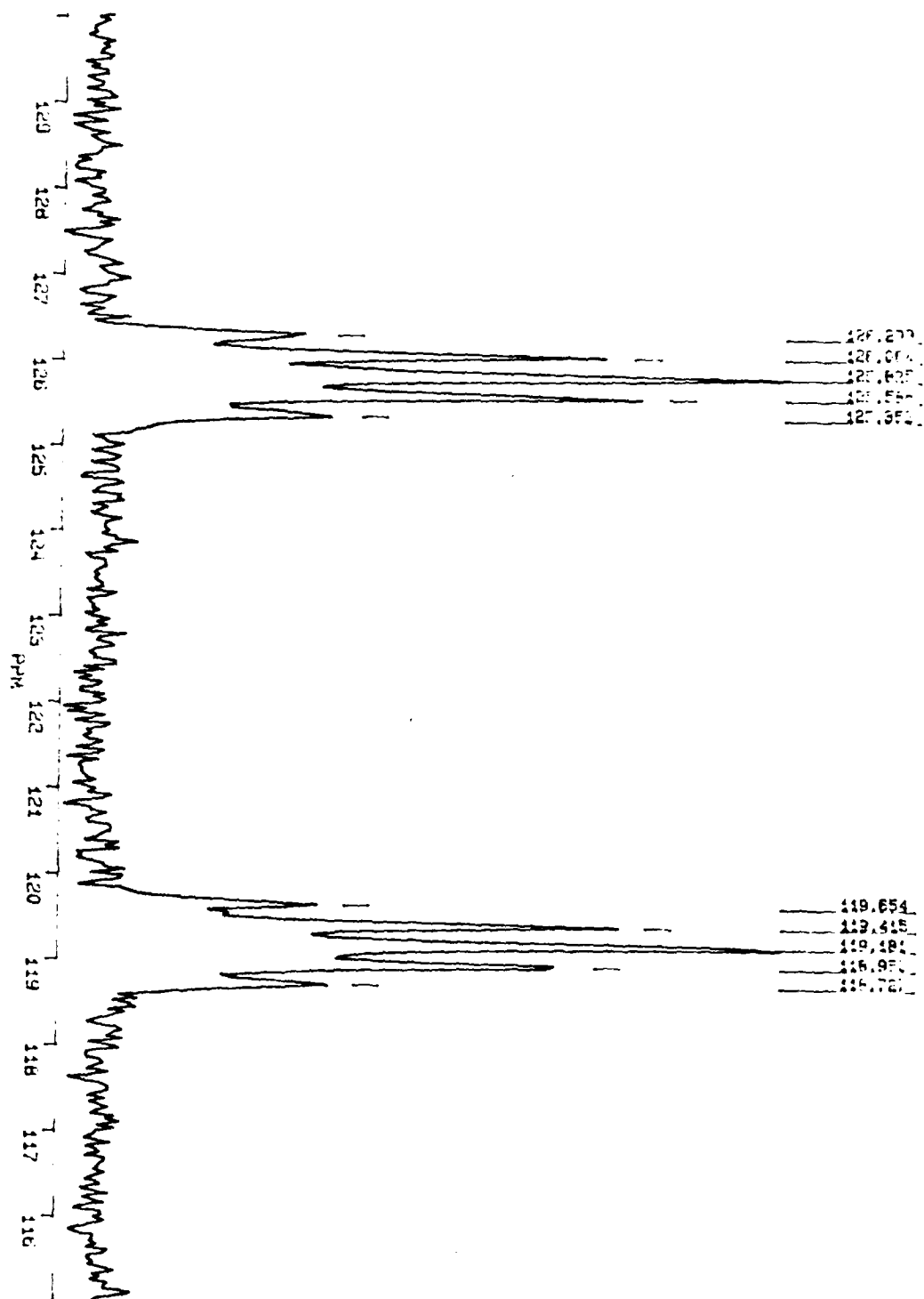


FIGURE 8.  $^{13}\text{C}$  NMR SPECTRUM OF CHLOROFUORODINITROMETHANE

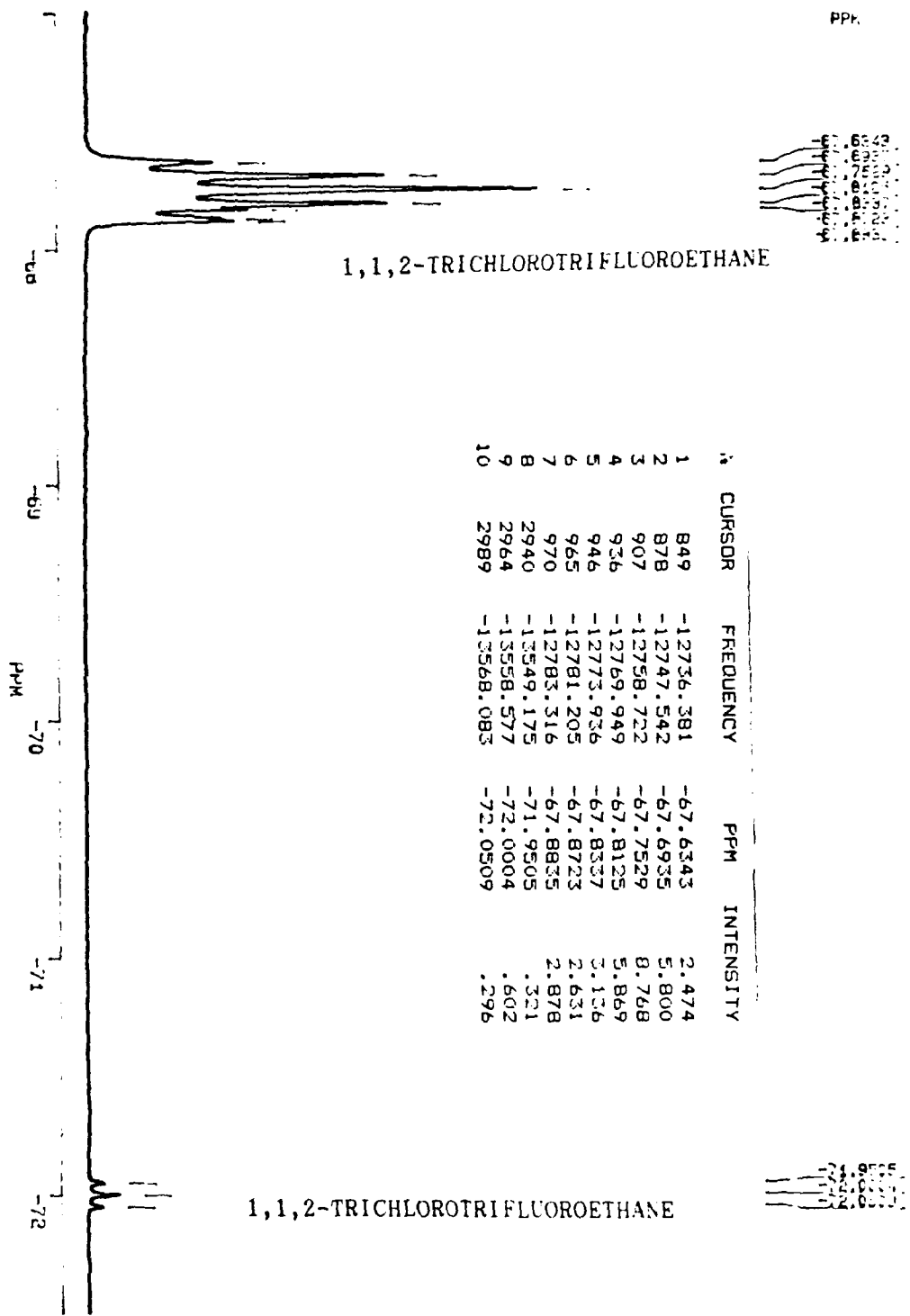
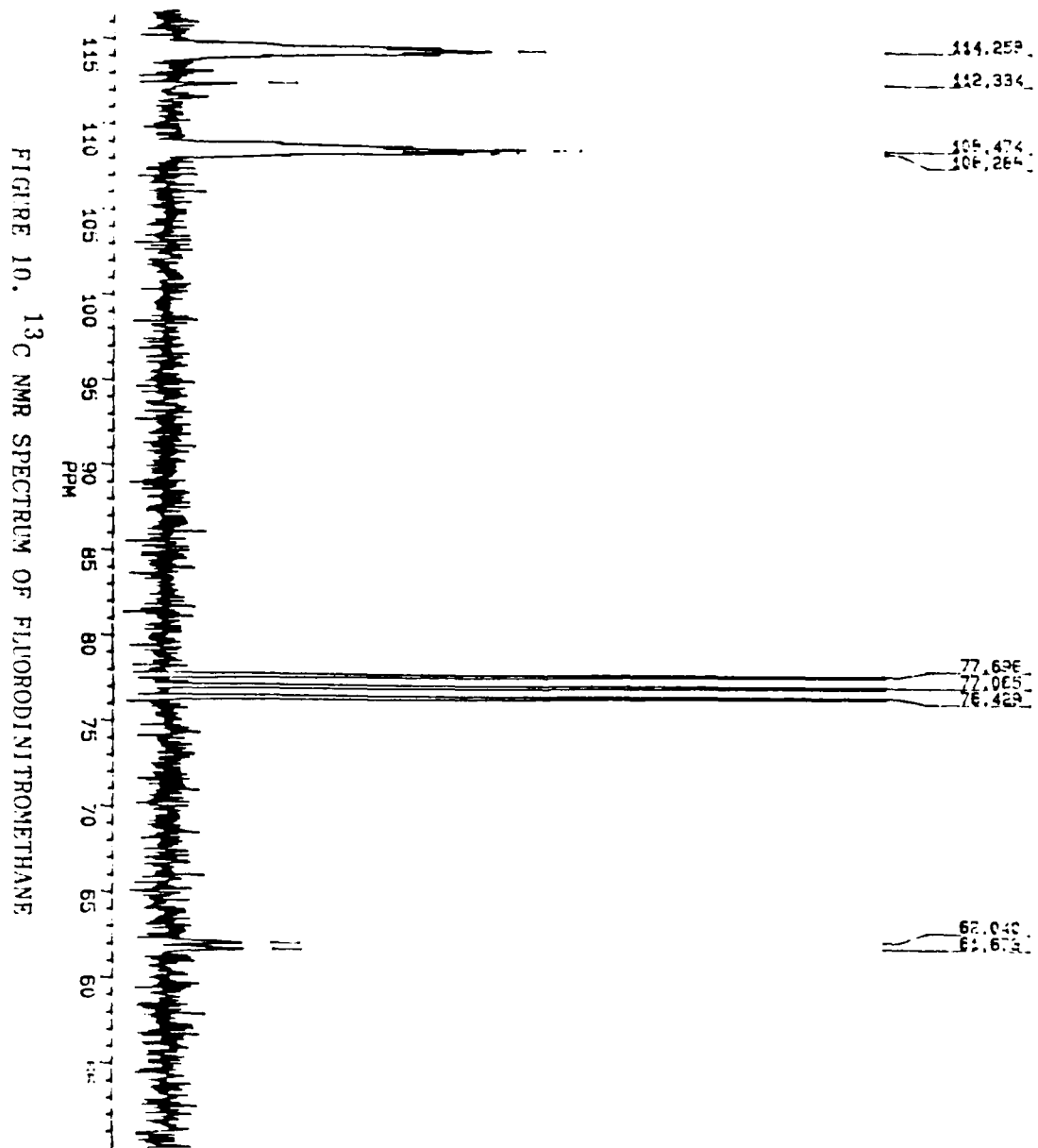


FIGURE 9.  $^{19}\text{F}$  NMR SPECTRUM OF CHLOROFUORODINITROMETHANE





Pr.

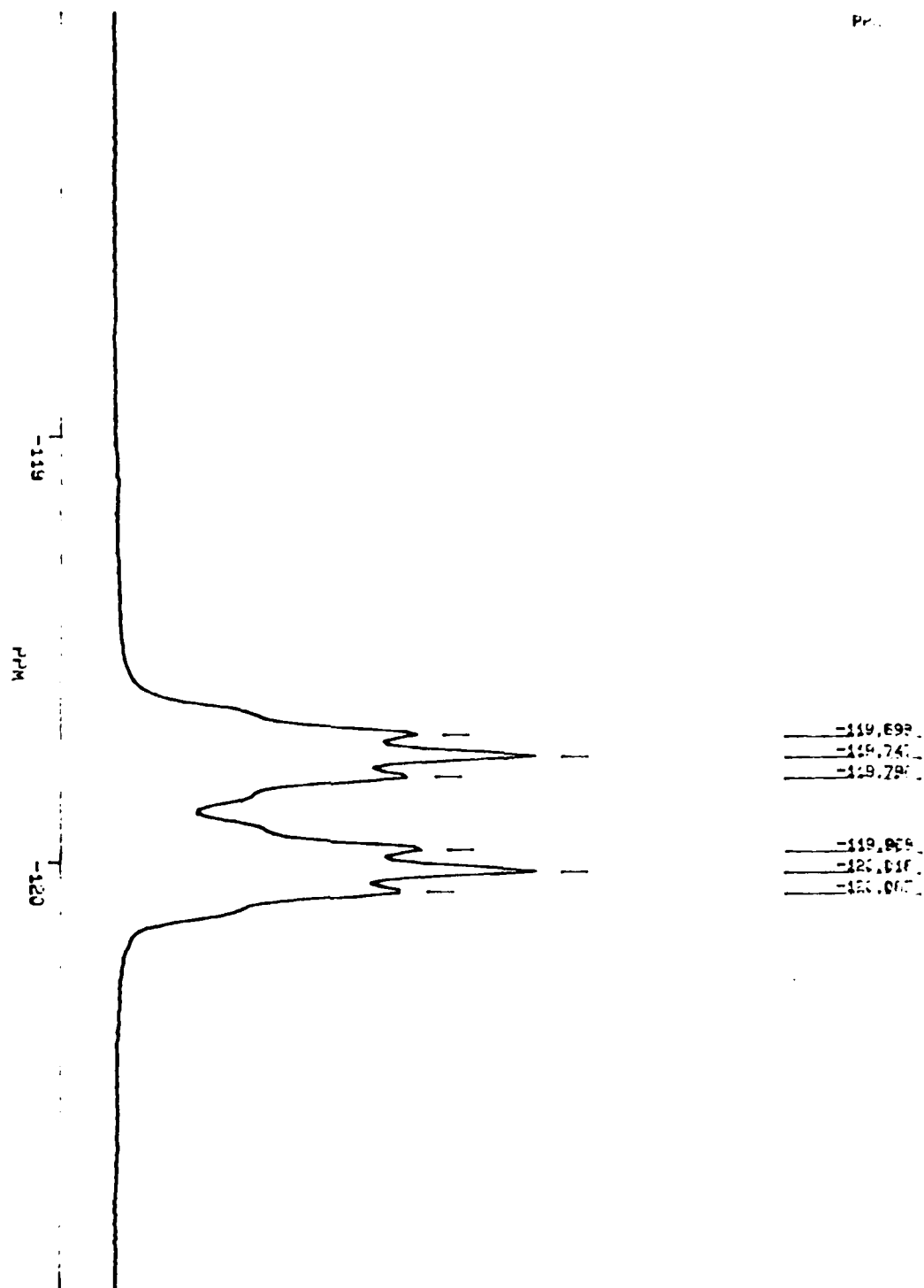


FIGURE 11.  $^{19}\text{F}$  NMR SPECTRUM OF FLUORODINITROMETHANE

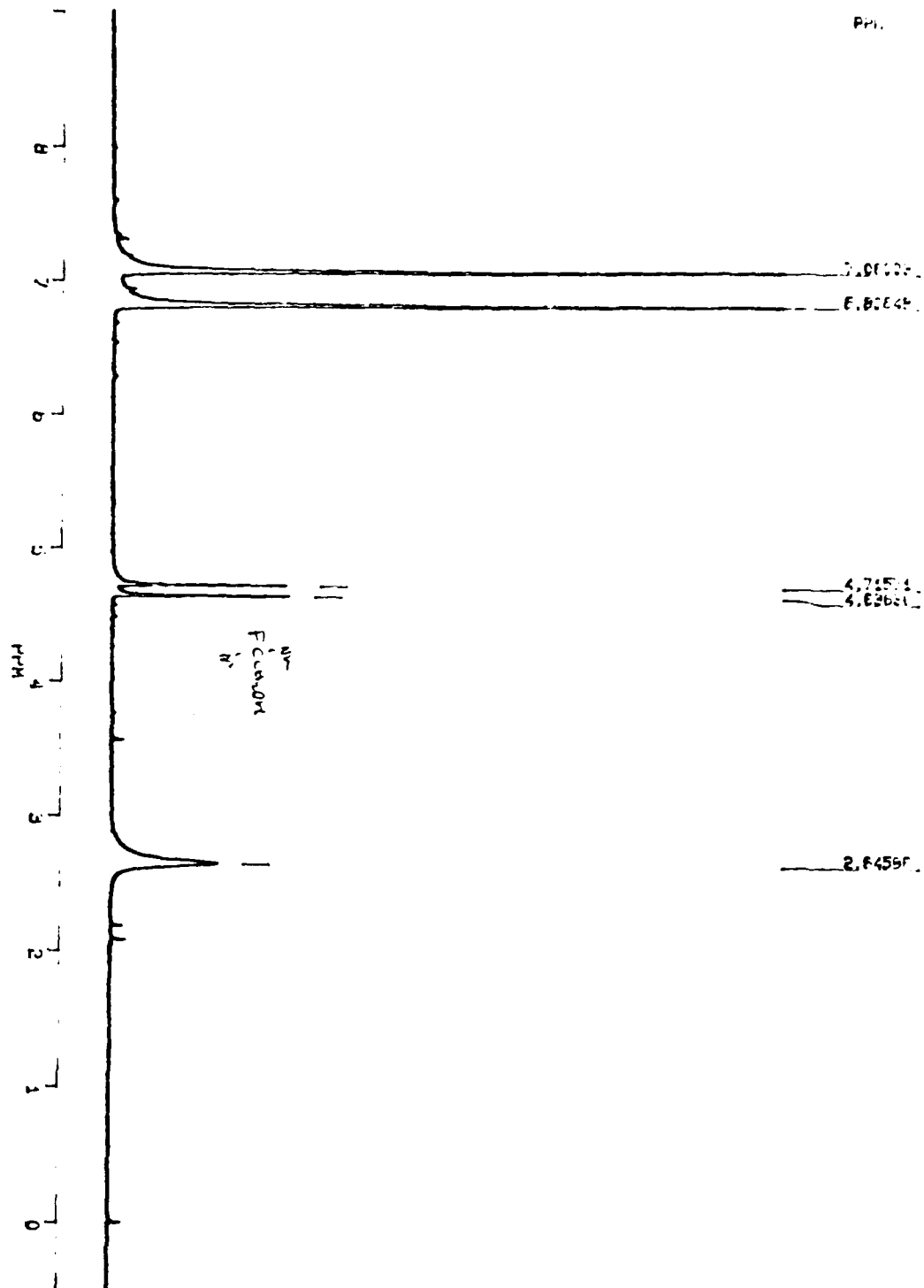


FIGURE 12.  $^1\text{H}$  NMR OF FLUORODINITROMETHANE AND FLUORODINITROETHANOL

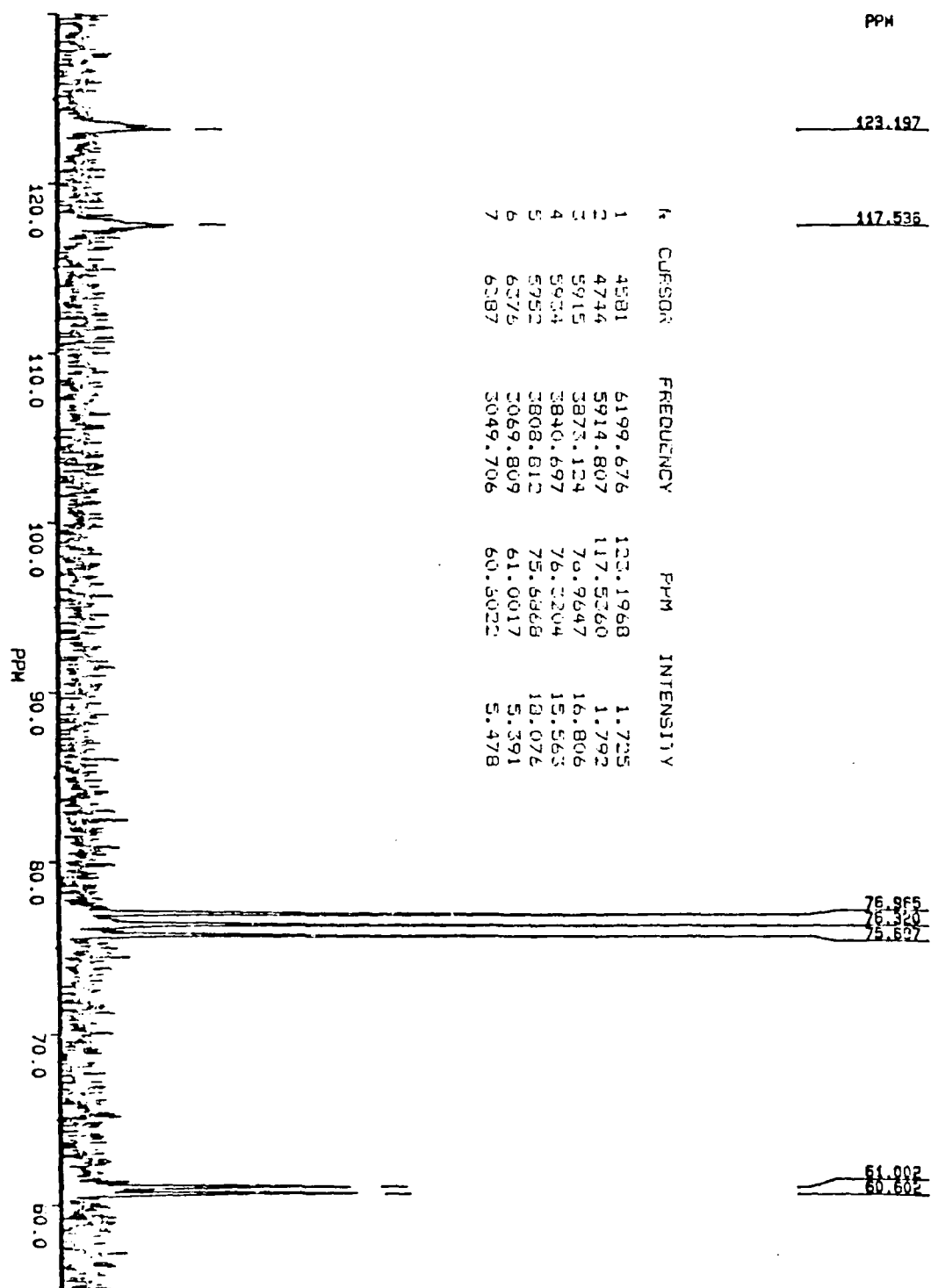


FIGURE 13.  $^{13}\text{C}$  NMR SPECTRUM OF FLUORODINITROETHANOL

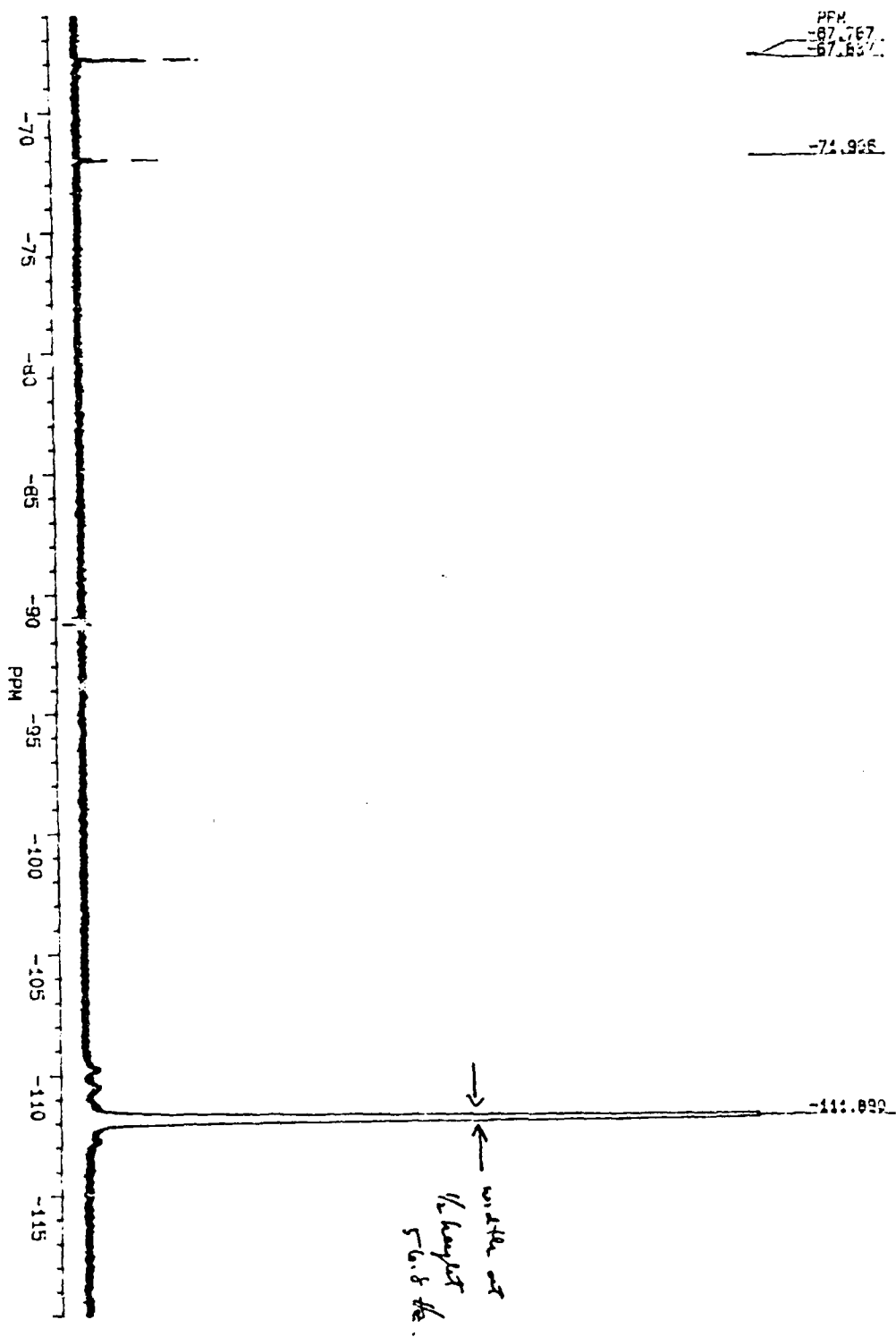


FIGURE 14.  $^{19}\text{F}$  NMR SPECTRUM OF FLUORODINITROETHANOL.

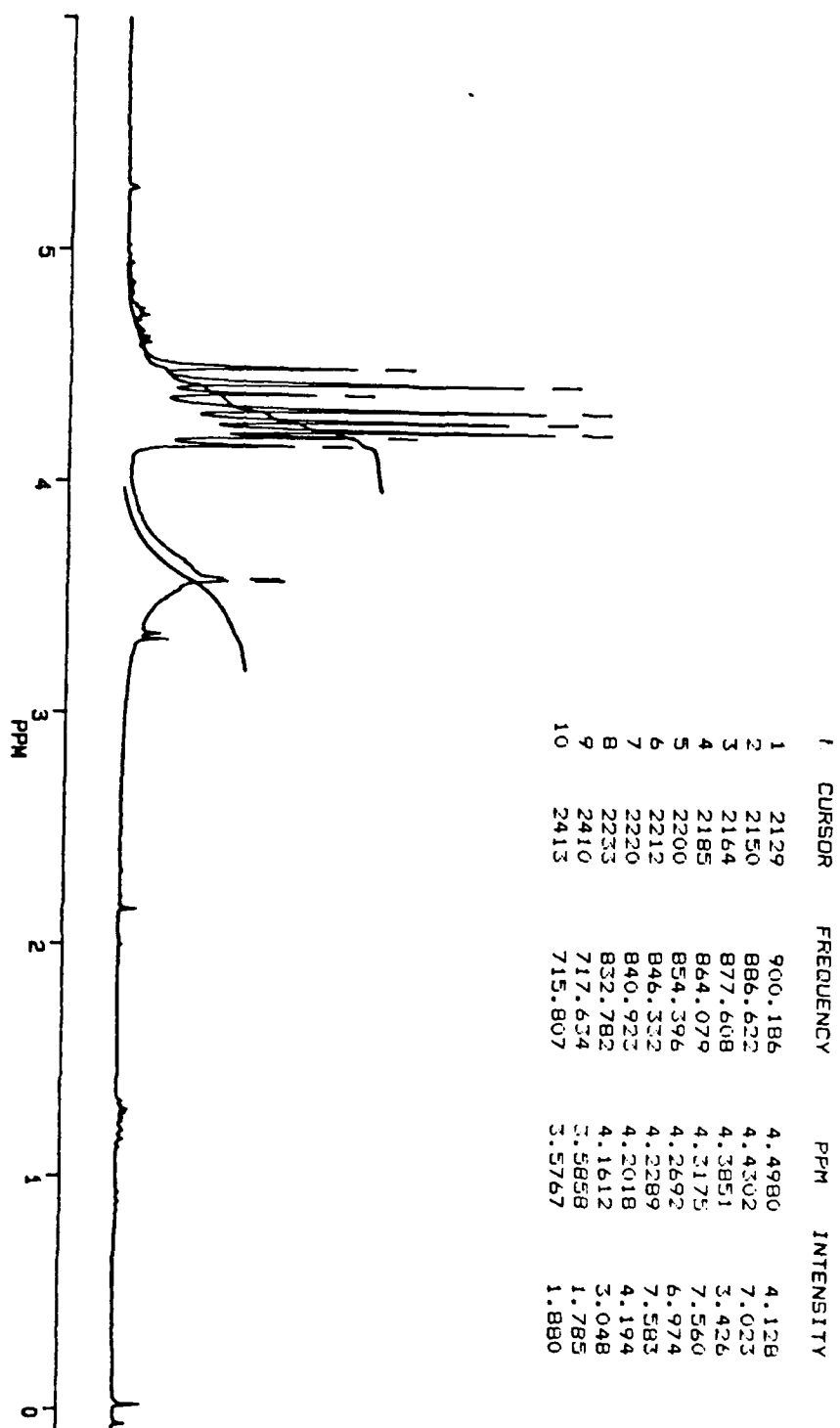


FIGURE 15.  $^1\text{H}$  NMR SPECTRUM OF CHLOROFLUORONITROETHANOL

n	CURSOR	FREQUENCY	PPM	INTENSITY
1	4611	6183.957	122.8845	1.034
2	5917	3906.185	77.6218	4.770
3	5925	3874.179	76.9858	4.093
4	5954	3841.918	76.3447	5.414
5	6237	3347.966	66.5291	16.573
6	6251	3324.329	66.0594	15.517

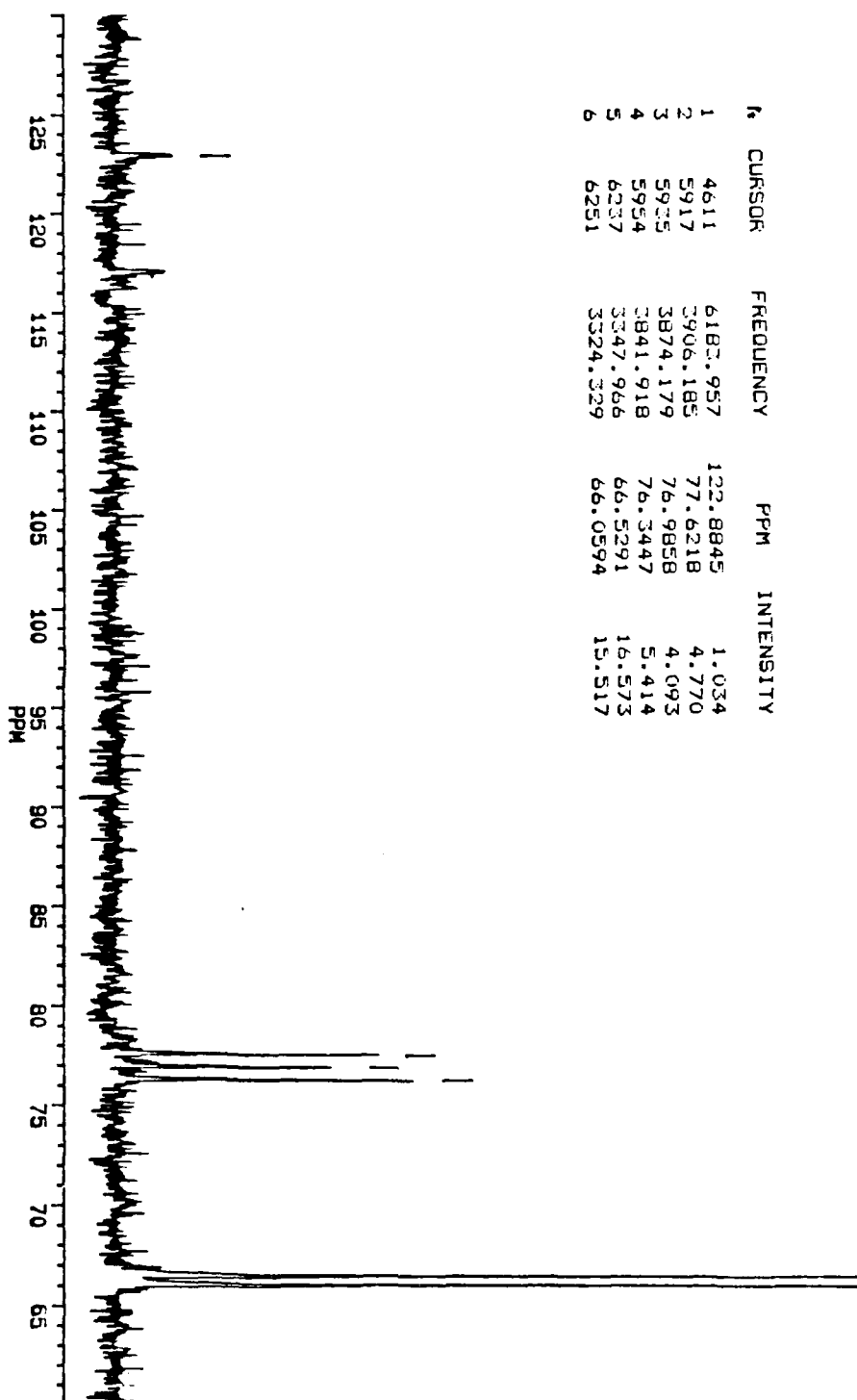


FIGURE 16.  $^{13}\text{C}$  NMR SPECTRUM OF CHLOROFLUORONITROETHANOL

h	CURSOR	FREQUENCY	PPM	INTENSITY
1	1824	-18476.538	-98.1163	7.922
2	1828	-18483.393	-98.1527	8.166
3	1837	-18498.672	-98.2339	7.989
4	1841	-18505.530	-98.2703	7.448

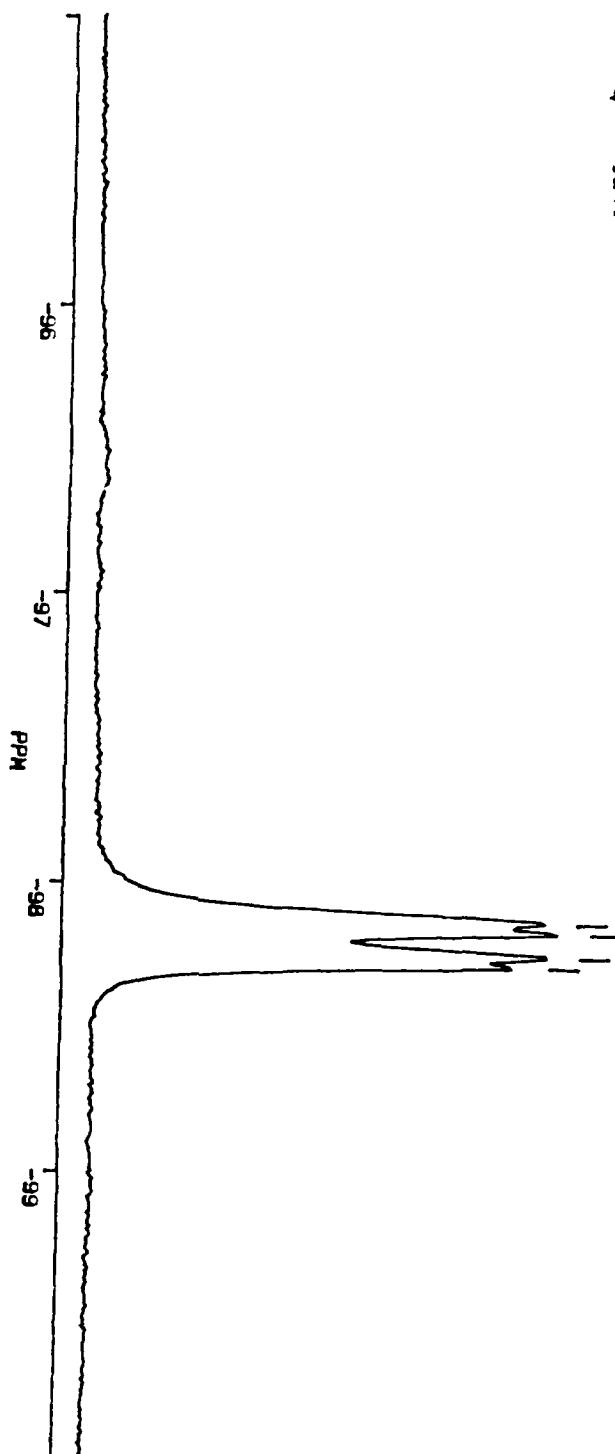


FIGURE 17.  $^{19}\text{F}$  NMR SPECTRUM OF CHLOROFUORONITROETHANOL



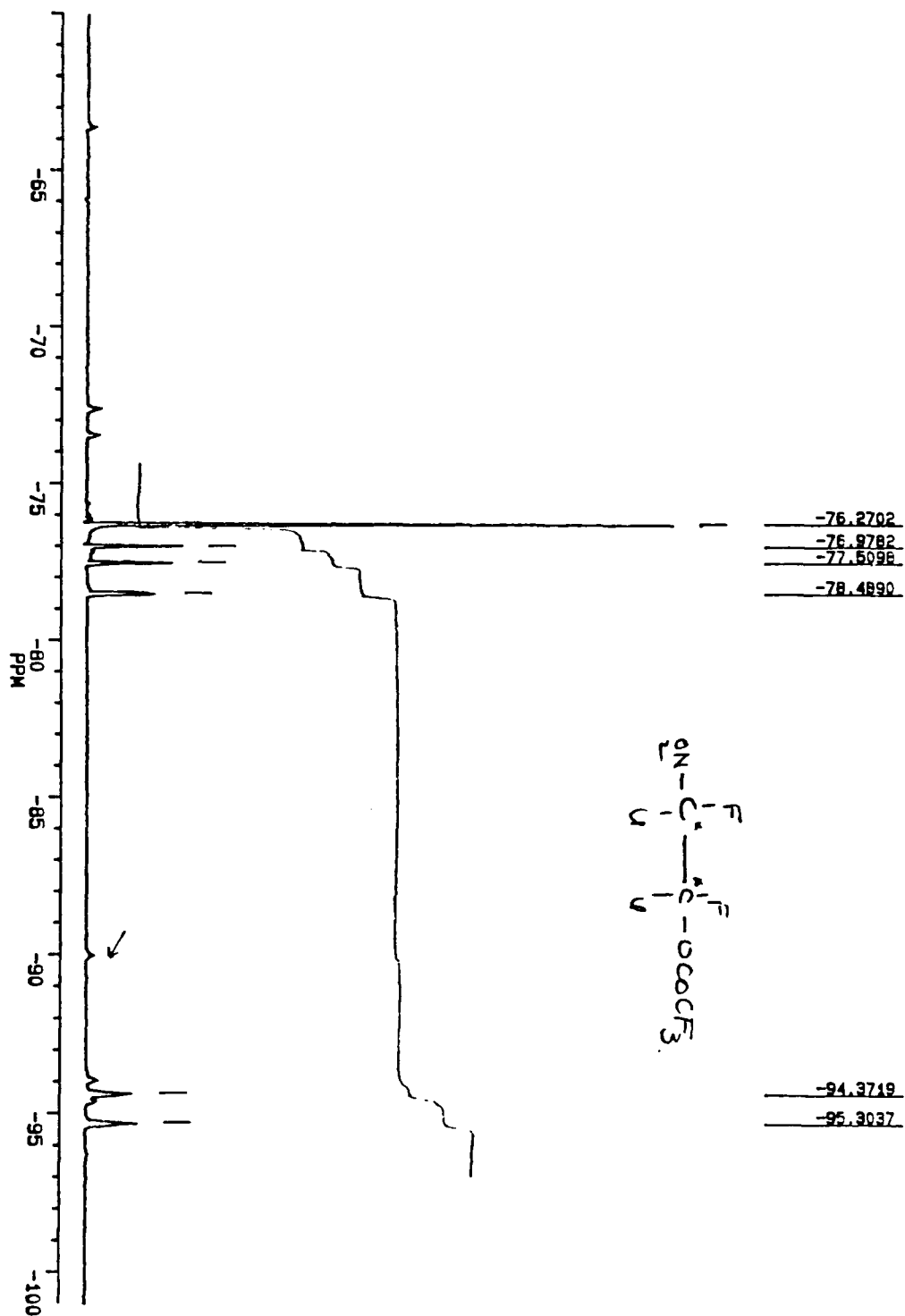


FIGURE 18.  $^{19}\text{F}$  NMR SPECTRUM OF 1,2-DICHLORO-1,2-DIFLUORO-2-NITRO-1-ETHANOL TRIFLUOROACETATE

FIGURE 19.  $^{19}\text{F}$  NMR SPECTRUM OF 1,2-DICHLORO-1,2-DIFLUORO-2-NITRO-1-ETHANOL  
TRIFLUOROMETHANESULFONATE

